Journal of Organometallic Chemistry, 65 (1974) 1—7

THE ORGANOMETALLIC CHEMISTRY OF THE ALKALINE EARTH METALS

II. CALCIUM DERIVATIVES OF INDENE, FLUORENE AND PHENYLACETYLENE FORMED BY METALATION WITH TRIPHENYLMETHYLCALCIUM CHLORIDE

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(Received May 23rd, 1973)

Summary

Triphenylmethylcalcium chloride has been used in metalation reactions to prepare new organocalcium compounds. Metalation of indene leads to the isolable complexes $(C_9H_7)_2CaL_2$ (L = tetrahydrofuran or L_2 = 1,2-dimethoxyethane) and sublimation of these complexes gives diindenylcalcium, $(C_9H_7)_2Ca$. Similar metalation of cyclopentadiene occurs. Fluorene and phenylacetylene are metalated in tetrahydrofuran to give $(C_{13}H_9)CaCl(THF)_2$ or $(C_6H_5C_2)CaCl\cdot xTHF$, respectively.

IR and ^1H NMR spectroscopic studies and other properties of the new products are discussed.

Introduction

Dicyclopentadienylcalcium has been well described in the literature [1] and has been shown to form complexes with oxygen and nitrogen ligands [2]. Analogues of dicyclopentadienylcalcium have received little attention. Thus, no characterised indenyl compound of calcium has been described and there has been one report only of an isolable fluorenyl compound, $(C_{13}H_9)_2Ca(THF)_2$ [3]. Kocheshkov and coworkers have shown that phenylcalcium iodide and diphenylcalcium, prepared in situ, do metalate indene and fluorene in solution but only the products of carbonation were identified [3,4].

Ethynyl compounds of calcium have also been reported recently. Bis(phenylethynyl)calcium, $(C_6H_5C_2)_2Ca$, has been prepared from calcium metal and the acetylene in liquid ammonia [5]. Ethynylcalcium iodide compounds, $(RC_2)CaI$ (R = C_6H_5, C_3H_7, C_4H_9, $EtOCH_2$) have been made by metalation with phenylcalcium iodide [6].

Triphenylmethylcalcium chloride was first prepared by Masthoff and

Krieg [7] and in subsequent papers they described reactions of this organometallic compound with compounds of the general formula R_xEH ($E = N, P$, As, O, S, Se, Cl) [8] but no reactions with hydrocarbons have been reported.

Results and discussion

Triphenylmethylcalcium chloride, as the bis(tetrahydrofuran) adduct, $(C_6H_5)_3CCaCl(THF)_2$, (I), was prepared from calcium amalgam and triphenylmethyl chloride in tetrahydrofuran [7]. The metalation reactions of (I) with the unsaturated hydrocarbons, indene, fluorene, cyclopentadiene and phenylacetylene have been investigated in tetrahydrofuran or 1,2-dimethoxyethane. The compounds diindenylcalcium and dicyclopentadienylcalcium (reaction 1) or fluorenylcalcium chloride and phenylethynylcalcium chloride (reaction 2) have been obtained as complexes with the ethereal solvents.

$$2(C_6H_5)_3CCaCl + 2RH \rightarrow R_2Ca + 2(C_6H_5)_3CH + CaCl_2 \qquad (1)$$

$$(R = C_9H_7, C_5H_5)$$

$$(C_6H_5)_3CCaCl + RH \rightarrow RCaCl + (C_6H_5)_3CH \qquad (2)$$

$$(R = C_{13}H_9, C_6H_5C_2)$$

Diindenylcalcium Complexes

The reaction of indene with (I) in tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) gives isolable colourless crystals of $(C_9H_7)_2Ca(THF)_2$, (II), or $(C_9H_7)_2Ca(DME)$, (III), respectively. The complexes were shown to have the assigned stoichiometry by metal analysis and by integration of their ^1H NMR spectra in pyridine-d_5 and benzene-d_6. They are extremely soluble in pyridine, where NMR evidence indicates that the ether ligands are displaced by the nitrogenous base, and also in tetrahydrofuran and 1,2-dimethoxyethane. They are soluble in benzene and toluene but insoluble in hexane. Under high vacuum, above 200°, the complexes sublime giving the free diindenylcalcium, $(C_9H_7)_2Ca$, (IV), after loss of ether. Compound (IV) is thermally stable, decomposing above 300°, and is negligibly soluble in benzene but sparingly soluble in ether.

The infrared spectra of complexes (II), (III) and (IV) show bands characteristic of the indenyl group. Compound (IV) shows no absorptions in the region 2840 - 3000 cm^{-1} and bands due to the free CH_2 group in free indene are absent. The C—H deformation found at 762 cm^{-1} in (IV) is shifted to lower wavenumber in (II) and (III) (748 cm^{-1}) and this may arise from a greater ionicity of the indenyl group in the latter complexes (cf. cyclopentadienyl compounds [9]). Bands assignable to ν(C—O—C) in (II) and (III) (1036 - 1024 cm^{-1} or 1061 cm^{-1} respectively) occur at lower frequencies than the same bands in the free ethers showing that there is a significant interaction between calcium and the oxygen ligand. The absence of bands in complex (III) between 864 - 996 cm^{-1} and the occurrence of a strong band at 864 cm^{-1}

TABLE 1

^{1}H NMR SPECTRA OF DIINDENYL CALCIUM COMPLEXES [a]

Compound	Solvent	Indenyl protons				Ether protons	
		4,7 [b]	5,6 [b]	2 [c]	1,3 [d]		
$(C_9H_7)_2Ca$	Et_2O	2.57	3.25	3.61	4.14		
	DME [e]	2.68	3.38	3.58	4.15		
	DME (–50°)	2.73	3.50	3.73	4.33		
$(C_9H_7)_2Ca(THF)_2$	C_6D_6	2.36	3.02	3.36	3.87	7.05 [f]	8.82 [g]
THF	C_6D_6					6.41 [f]	8.56 [g]
$(C_9H_7)_2Ca(DME)$	C_6D_6	2.51	3.14	3.23	3.88	7.85 [h]	7.61 [j]
DME	C_6D_6					6.64 [h]	6.86 [j]
$(C_9H_7)_2Ca(THF)_2$/DME (1/7.8)	C_6D_6	2.49	3.14	3.22	3.87	6.43 [f] 6.79 [h]	8.55 [g] 6.94 [j]

[a] Resonances in τ(ppm) relative to TMS as internal standard.
[b] Two parts of AA′BB′ multiplet.
[c] Triplet.
[d] Doublet.
[e] 1,2-Dimethoxyethane.
[f] THF α-H.
[g] THF β-H.
[h] DME — CH_2.
[j] DME — CH_3.

suggest that 1,2-dimethoxyethane adopts a *gauche* conformation [10] and that it is bidentate.

The ^{1}H NMR spectrum of (IV) in diethyl ether shows only resonances assignable to the indenyl group (see Table 1). Similar spectra have been observed for Group IA metal indenyl compounds [11]. In the spectrum of (IV) [or (III)] in 1,2-dimethoxyethane at 35° it is interesting that the relative shifts of the 2 and the 5,6 hydrogen resonances are reversed compared to the same resonances in indenylsodium and indenylpotassium [11]. This may be due to the larger formal charge on the Group II metal or to the proximity of two indenyl moieties.

On cooling, the ^{1}H NMR spectrum of indenyllithium in 1,2-dimethoxyethane at −40° shows a larger upfield shift of the resonances of the hydrogens attached to the C_6 ring relative to those of the C_5 ring. Such shifting does not occur for (C_9H_7)Na or (C_9H_7)K and a proposed explanation for this is that the Li atom (ion) is located over the C_6 ring whereas Na or K is over the C_5 ring [11]. The spectrum of $(C_9H_7)_2$Ca in 1,2-dimethoxyethane on cooling to −50° shows no marked shifting so that it may be tentatively proposed that the Ca atom (ion) is predominantly over the C_5 ring. At −50° all resonances of $(C_9H_7)_2$Ca show slight upfield shifts in 1,2-dimethoxyethane and this is probably caused by a slight increase in metal ion solvation at the lower temperatures.

The ^{1}H NMR spectra of the complexes (II) and (III) in benzene-d_6 are of interest. The resonances of the tetrahydrofuran or 1,2-dimethoxyethane ligands show marked upfield shifts and the relative positions of the CH_3 and CH_2 hydrogen resonances in (III) are reversed, compared to the free ligands. Thus the ether ligands are still bound to Ca in solution. Simple coordination of ether to a metal should cause a downfield shift of α-hydrogen resonances so that the opposite effect probably arises from interaction with the indenyl ligands. Similar effects have been observed for non-stoichiometric complexes of fluorenyllithium with tetrahydrofuran and 1,2-dimethoxyethane [12].

The addition of an approximately eightfold molar quantity (7.8 by integration) of 1,2-dimethoxyethane to (II) in benzene-d_6 displaces entirely the coordinated tetrahydrofuran as indicated by the ^{1}H NMR spectrum (reaction 3). The resonances of 1,2-dimethoxyethane, however, are shifted to somewhat higher fields than for the free ether, and the indenyl resonances occur at the same τ values as for (III) in C_6D_6. Assuming that only one molecule of 1,2-dimethoxyethane is bound to Ca in solution then exchange (4) is occurring. The assumption is supported by the calculated shifts for 1,2-dimethoxyethane undergoing fast exchange. (Calculated: CH_2, τ 6.79; CH_3, 6.96 ppm. Observed: CH_2, τ 6.79; CH_3, 6.94 ppm.)

$$(C_9H_7)_2Ca(THF)_2 \xrightarrow[\text{excess}]{\text{DME}} (C_9H_7)_2Ca(DME) + 2\,THF \qquad (3)$$

$$(C_9H_7)_2Ca(DME) + x\,DME \rightleftharpoons (C_9H_7)_2Ca(DME) + x\,DME \qquad (4)$$

Dicyclopentadienylcalcium

Metalation of cyclopentadiene by compound (I) in 1,2-dimethoxyethane gives dicyclopentadienyl(1,2-dimethoxyethane)calcium, $(C_5H_5)_2Ca(DME)$, (V) [2].

The reaction between (III), in excess, and cyclopentadiene in 1,2-dimethoxyethane was studied by ^{1}H NMR spectroscopy. Exchange (5) took place over 10 min. The product, (V), was monitored by the appearance of the C_5H_5 resonance signal and it was formed in virtually 100% yield.

$$2C_5H_6 + (C_9H_7)_2Ca \rightarrow (C_5H_5)_2Ca + 2C_9H_8 \qquad (5)$$

Fluorenylcalcium chloride

Fluorenylbis(tetrahydrofuran)calcium chloride, $(C_{13}H_9)CaCl(THF)_2$, (VI), is formed as a yellow crystalline solid by metalation of fluorene with compound (I). Complex (VI) is sparingly soluble in tetrahydrofuran and 1,2-dimethoxyethene and insoluble in benzene. Hydrolysis liberates free fluorene, and carboxylation in tetrahydrofuran at −78° yields 9-fluorene-carboxylic acid almost quantitatively. On prolonged heating in tetrahydrofuran at 63° and subsequent carbonation, minor amounts of 9-fluorenone and free fluorene are isolated with 9-fluorenecarboxylic acid.

The IR spectrum of (VI) (see Experimental Section) shows band assignable to the $C_{13}H_9$ ligand and coordinated tetrahydrofuran [ν(C—O—C)1038 cm^{-1}]. The complex is insufficiently soluble for ^{1}H NMR spectroscopy but exchange reactions between an excess of (VI) and cyclopentadiene or indene in 1,2-dimethoxyethane are shown to occur giving (V) or (III), respectively, as observed by their ^{1}H NMR spectra.

Phenylethynylcalcium chloride

Metalation of phenylacetylene with compound (I) in tetrahydrofuran yields, after recrystallisation, phenylethynylcalcium chloride as an adduct with tetrahydrofuran of approximate formula $(C_6H_5C_2)CaCl\cdot(0.8\ THF)$, (VII). The tetrahydrofuran is not removed under high vacuum at room temperature and higher temperatures lead to some decomposition on the loss of the ether as indicated by IR spectroscopy. The product (VII) is only sparingly soluble in tetrahydrofuran or 1,2-dimethoxyethane so that ^1H NMR spectroscopy can not be used. The product is air sensitive and hydrolysis produces free phenylacetylene. The IR spectrum of (VII) shows bands assignable to the acetylene ligand [e.g. $\nu(C{\equiv}C)2019\ cm^{-1}$] and tetrahydrofuran.

Other reactions of calcium

In attempts to prepare benzyl- or diphenylmethyl-calcium compounds analogous to (I), benzyl chloride or benzhydryl chloride was treated with calcium amalgam in tetrahydrofuran at and below room temperature. In reactions with benzhydryl chloride a pink-coloured product is obtained but this colour was rapidly discharged on attempted purification and this may indicate an unstable organometallic compound. From either reactant a high yield of the coupled hydrocarbon, bibenzyl or 1,1,2,2-tetraphenylethane, respectively, is isolated.

Experimental

Solvents and calcium metal were treated as described previously [2]. Indene and phenylacetylene were dried over 5A molecular sieves and distilled before use. Fluorene was sublimed before use.

Calcium was determined by EDTA titration and chloride gravimetrically as AgCl. IR spectra were recorded in KBr with a Perkin - Elmer 457 spectrometer, and ^1H NMR spectra with a 60 MHz Perkin - Elmer R 12 spectrometer operating at 35° unless otherwise stated.

$[(C_6H_5)_3C]CaCl(THF)_2$, (I), was prepared from triphenylmethyl chloride and calcium amalgam in tetrahydrofuran according to the method of Masthoff and Krieg [7]. (Found: Ca, 8.3. $C_{27}H_{31}O_2ClCa$ calcd.: Ca, 8.7%.)

Diindenylbis(tetrahydrofuran)calcium

Indene (1.0 g) was distilled in vacuo into a stirred suspension of (I) (1.8 g) in tetrahydrofuran (30 ml) at −20°. The stirring was continued for 30 min. Filtration, followed by reduction in volume of the filtrate and cooling to −40° gave colourless crystals. The crystals were separated washed and dried, 10^{-3} mmHg. Yield ca. 65%; m.p. 165°. (Found: Ca, 9.7. $C_{26}H_{30}O_2Ca$ calcd.: Ca, 9.7%.) Major IR bands: 3047 w, 2965 m, 1334 m, 1324 s, 1255 m, 1036 s, 1024 s, 874 m, 748 vs, 441 m, 380 (br)m cm^{-1}.

Diindenyl(1,2-dimethoxyethane)calcium

In a similar experiment to the above indene (0.8 g) and (I) (1.5 g) in 1,2-dimethoxyethane (30 ml) gave colourless crystals in ca. 50% yield (m.p. 138°). (Found: Ca, 11.2. $C_{22}H_{24}O_2Ca$ calcd.: Ca, 11.1%.) Major IR bands: 3054 w, 1320 s, 1252 s, 1213 m, 1183 m, 1102 m, 1061 s, 864 s, 748 vs, 437 m, 280 (br)m cm^{-1}.

Diindenylcalcium

Sublimation of diindenylbis(tetrahydrofuran)calcium [or diindenyl(1,2-dimethoxyethane)calcium] in vacuo, 10^{-3} mmHg, above 200° gave the product as colourless crystals on the colder parts of the tube. Yield ca. 50%, m.p. $>$ 300° (dec.). IR spectrum: 3059 m, 3024 (sh), 1392 w, 1337 (sh), 1327 s, 1253 w, 1217 w, 1116 w, 1075 (br)w, 1034 w, 997 w, 789 s, 762 vs, 736 (sh), 717 w, 438 m, 386 w, 295 (br)m cm^{-1}.

Fluorenylbis(tetrahydrofuran)calcium chloride

Fluorene (0.6 g) in tetrahydrofuran (20 ml) was added dropwise to a stirred suspension of (I) (1.5 g) in tetrahydrofuran (80 ml) at ambient temperature. A yellow precipitate was formed immediately. Filtration, followed by washing with tetrahydrofuran and drying, 10^{-3} mmHg, gave the product in 88% yield. (Found: Ca, 10.5; Cl, 9.5. $C_{21}H_{25}O_2ClCa$ calcd.: Ca, 10.4; Cl, 9.2%.) Major IR bands: 3030 w, 2963 m, 2869 m, 1444 m, 1316 m, 1219 m, 1038 s, 878 m, 735 vs, 677 m, 330 (br)m cm^{-1}.

Carboxylation of fluorenylbis(tetrahydrofuran)calcium chloride

Carbon dioxide was bubbled slowly into a suspension of $(C_{13}H_9)$-$CaCl(THF)_2$ in tetrahydrofuran for 30 min at −78°. Acidification and a standard extraction procedure gave crystals of 9-fluorenecarboxylic acid, yield 94%, m.p. 219°.

Reaction of (I) with cyclopentadiene

Cyclopentadiene (0.16 g) was distilled, under vacuum, into a stirred suspension of (I) (0.1 g) in 1,2-dimethoxyethane (15 ml) at −10°. After 30 min the solution was filtered and hexane (30 ml) was added to the filtrate at −30°. Colourless crystals of dicyclopentadienyl(1,2-dimethoxyethane)calcium, $(C_5H_5)_2Ca(C_4H_{10}O_2)$, (55%) were obtained and identified by IR and NMR spectroscopy.

Reaction of (I) with phenylacetylene

Phenylacetylene (0.44 g) was distilled, under vacuum, into a stirred suspension of (I) (1.16 g) in tetrahydrofuran (25 ml) at −35° and the reaction mixture was then allowed to warm to room temperature. Filtration gave a light pink, sparingly soluble solid (0.33 g). Extraction of this solid with tetrahydrofuran (45°), followed by filtration, reduction in volume and addition of hexane gave a small quantity of off-white solid (ca. 40 mg) which was washed and dried under vacuum (10^{-3} mmHg). (Found: Ca, 17.3. $C_8H_5CaCl{\cdot}0.8\ C_4H_8O$ calcd.: Ca, 17.1%.) Major IR bands: 3043 w, 2019 w, 1482 m, 1441 m, 1189 m, 1030 (br)m, 751 vs, 686 s, 540 m, 491 m cm^{-1}.

Reactions of calcium amalgam

(a). With benzhydryl chloride. Calcium amalgam (1.1 g Ca) was shaken with a solution of benzhydryl chloride (1.1 g) in 1,2-dimethoxyethane (50 ml) for 4 h at −12°. Filtration gave calcium chloride as the 1,2-dimethoxyethane adduct and evaporation of the filtrate gave crystals of 1,1,2,2-tetraphenylethane, yield 75%, m.p. 209°.

(b). With benzyl bromide. In a similar reaction to the above in tetrahydrofuran, benzyl bromide and calcium amalgam at room temperature gave dibenzyl, 90%, m.p. 51°.

Acknowledgement

We thank the International Synthetic Rubber Co. Ltd. for a grant in support of these investigations.

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